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Cyclopentenone Synthesis from 1,1-Dichloroallyllithium-Ketone Adducts as Well as from Dichlorocarbene-Allyl Alcohol Adducts

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Treatment of (3,3-dialkyl-2,2-dichlorocyclopropyl)methanols with hydrobromic acid gives 2-cyclopentenones through postulated intermediates, 3-chlorocyclopentadienyl cations. Another method which should give the same cationic intermediates involves trifluoroacetic acid catalyzed reaction of 3,3-dichloro-1-alken-4-ols. This is found to be particularly useful for cyclopentenone annulation.

The construction of five-membered carbocyclic system is important in the synthesis of physiologically active natural products.[1] We wish to describe two new methods based on the thermal conrotatory ring-closure of 3-chloropentadienyl cation.[2]

During the course of the study of carbenoid chemistry,[3] it was found that dichlorocarbene generated by the phase-transfer technique[4] adds efficiently to allyl alcohols, in contrast to the previous observation by Seyferth and Mai.[5] For example, 4-methyl-3-penten-2-ol was converted into the dichlorocyclopropane **1** in 92% yield without appreciable deoxygenation[6] or chlorination.[7] When the adduct **1** was heated in 47% hydrobromic acid at 100 °C, 3,5-dimethyl-2-cyclopentenone (**2**)[8] was produced in 83% yield. Application of this procedure to various allyl alcohols **3** gave 2,3-disubstituted 2-cyclopentenones **5** (Table 1).

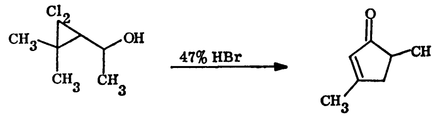
TABLE 1. SYNTHESIS OF 2-CYCLOPENTENONES FROM ALLYL ALCOHOLS

Allyl Alcohol	Dichlorocyclopropane[a] %yield	Cyclopentenone[b] % yield
3a	**4a**, 79	**5a**,[c] 44
3b	**4b**, 79	**5b**,[d] 56
3c	**4c**, 60	**5c**,[d] 59
3d	**4d**, 77[e]	**5d**,[f] 76

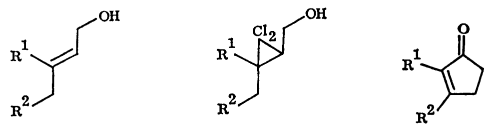
a) Dichlorocarbene was generated by the phase-transfer technique. b) The (dichlorocyclopropyl)methanol **4** was heated in hydrobromic acid at 100 °C for several hours unless otherwise specified. c) Ref. 28. d) Ref. 24. e) Alcohol was converted into α-ethoxyethyl ether before the dichlorocarbene addition and afterwards the protecting group was removed. f) Heating **4d** in trifluoroacetic acid under reflux for 90 h.

Although the dichlorocarbene addition generally proceeds well,[9] the yield of the particular adduct **4d** was very unsatisfactory, the overall yield of **5d** being only 37%.[2a] However, the yields were much improved by protecting the hydroxyl group with ethyl vinyl ether. Protection, dichlorocarbene addition and regeneration of the hydroxyl group[10] gave **4d** in 77% isolated yield. Subsequent acid treatment of **4d** was best performed with trifluoroacetic acid (TFA) which was found to be a less reactive reagent than hydrobromic acid but far more selective to give the desired enone **5d** in 76% yield.

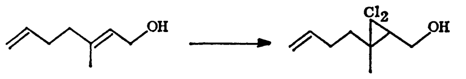
The cyclopropylmethanol **7** obtained by selective :CCl_2 addition to the allyl alcohol **6**[4] was transformed into 2-methyl-3-(*trans*-1-propenyl)-2-cyclopentenone (**9**). Under these acidic conditions the anticipated cyclopentenone **8** isomerized to the conjugated dienone **9**.



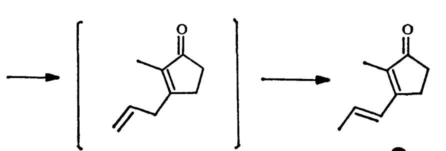
1 **2**



3 **4** **5**



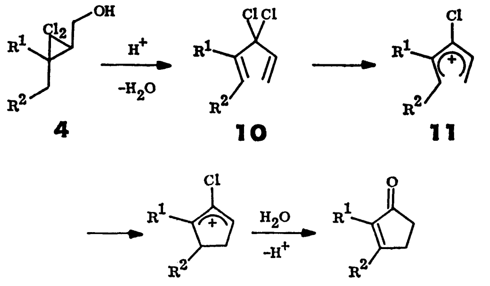
6 **7**



8 **9**

a, $R^1=CH_3$, $R^2=H$
b, $R^1=CH_3$, $R^2=n\text{-}C_4H_7$
c, $R^1=CH_3$, $R^2=n\text{-}C_5H_{11}$
d, R^1, $R^2=\text{-}(CH_2)_{10}\text{-}$

The mechanism of the cyclopentenone formation can be rationalized by Scheme 1. Conjugate dehydration of **4** gives a dichlorodiene **10**, which undergoes solvolysis to yield a chloropentadienyl cation **11**. Thermal conrotatory ring closure of **11** gives a chlorocyclopentenyl



12 **5**

Scheme 1.

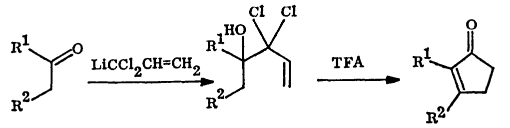
cation **12**, deprotonation followed by hydrolysis giving the cyclopentenone **5**. Noteworthy is the regiochemistry of the reaction. Heating **4b** in hydrobromic acid afforded 3-butyl-2-methyl-2-cyclopentenone (**5b**) exclusively, and none of the corresponding isomer, 2-pentyl-2-cyclopentenone was detected. It should be noted that the original methyl group is not incorporated into the five-membered ring and a long alkyl appendage resides at the C(3) position. The initial dehydration of **4** and the final deprotonation in **12** are controlled to give the more substituted olefins.(11)

In order to confirm the above mechanism we chose a dichlorohomoallyl alcohol (Scheme 2) as an alternative precursor of the intermediates **10**—**12**. The dichlorohomoallyl alcohol **14** was prepared according to the reported method.(12) Thus, 1,1-dichloroallyllithium was prepared *in situ* and directly allowed to react with ketone by adding lithium diisopropylamide to a mixture of a ketone and 3,3-dichloropropene. The adduct was successively subjected to acidic conditions. First we studied the conversion of **13d** into **5d** and found that various acids are effective. Acid, conditions, and % yield were: hydrobromic acid–acetic acid, reflux, 3 h, 55; titanium tetrachloride-dichloromethane, room temp, 3 h, 81; TFA, reflux, 1.5 h, 89; TFA, room temp, 1.5 h, 90. Thus, under the last condition **13c**—**g** were transformed into **5**. The results are summarized in Table 2.

TABLE 2. CYCLOPENTENONE ANNULATION

Ketone	Dichlorohomoallyl alcohol,a) % yield	Cyclopentenoneb) % yield
13c	**14c**, 73	**5c**, 87
13d	**14d**, (66)c)	**5d**,d) 90
13e	**14e**, 68	**5e**,d) 80
13f	**14f**, 63	**5f**,e) 87
13g	**14g**,f) 56	**5g**,g) 71

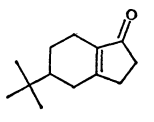
a) The adducts were obtained by adding 1.5 equivalents of lithium diisopropyl amide to a mixture of **13** and 3,3-dichloropropene (1.5equiv) in tetrahydrofuran at −78°C. See Ref. 12a. b) Transformation of **14** to **5** was carried out in TFA at room temperature for a couple of hours. c) The yield was taken from Ref. 12a. d) Ref. 25. e) Ref. 26. f) This compound was synthesized by Seyferth *et al.* (Ref. 12b) using dichloroallyllithium generated by transmetallation. g) Ref. 27.



c, $R^1=CH_3$, $R^2=n\text{-}C_5H_{11}$
d, R^1, $R^2=\text{-}(CH_2)_{10}\text{-}$
e, R^1, $R^2=\text{-}(CH_2)_6\text{-}$
f, R^1, $R^2=\text{-}(CH_2)_5\text{-}$
g, R^1, $R^2=\text{-}(CH_2)_4\text{-}$

Scheme 2.

Apparently the two step procedure is applicable to both cyclic and acyclic ketones and particularly efficient for cyclopentenone annulation. Although cationic intermediates are involved in the reaction sequence, transannular by-path(13) is negligible in the cyclization of the medium-ring compound **14e** which gives cyclopentenone **5e** in 54% overall yield. The two step process makes 5-substituted tetrahydroindanone derivatives more readily accessible as illustrated for the synthesis of **15** (55% overall yield) from 4-*t*-butylcyclohexanone.



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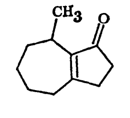

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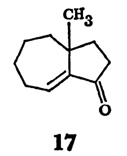

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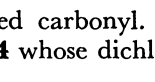
Regioselectivity of the cyclopentenone formation depends on the structure of the substrate. 2-Octanone was converted into 2-methyl-3-pentyl-2-cyclopentenone (**5c**) exclusively. The selectivity may be explained in terms of the favored formation of the more substituted olefin at the dehydration step. On the other hand, when 2-methylcycloheptanone–dichloroallyllithium adduct was subjected to the annulation reaction, only **16** was produced with no trace of its isomer **17**.(14–16)

The key of the cyclopentenone annulation is the addition of 1,1-dichloroallyllithium at C(1) carbon. Although Seyferth *et al.*(12b) suggested that the regioselectivity of the addition of the lithium reagent to ketones or aldehydes is controlled by electronic rather than steric factor, 2-methylcyclohexanone gave only the adduct **18** in contrast to cyclohexanone or 2-methylcycloheptanone. Thus, steric hindrance as well as ring size(17) appear to determine the regiochemistry of the addition. TFA catalyzed reaction of **18** gave cyclopentenone **19**(18) in 47% yield.



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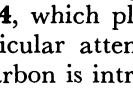

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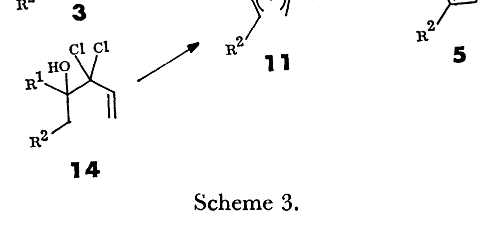
The two cyclopentenone forming reactions are summarized in Scheme 3. Both **3** and **14** give a common intermediate **11** and finally cyclopentenone **5** upon acid treatment. The carbonyl carbon of **5** originates from *gem*-dichloro carbon of **3** and **14**, which plays the role of a protected carbonyl. Particular attention should be paid to **14** whose dichloro carbon is introduced as a



Scheme 3.

TABLE 3. PHYSICAL PROPERTIES OF (DICHLOROCYCLOPROPYL)METHANOLS AND CYCLOPENTENONES

Compound	Bp (°C/Torr)[a]	IR(cm^{-1})[b]	PMR(δ)[c]
4a[d]	110—120/35	3400, 1145, 1084, 1030, 850, 820, 805	1.20(s, 3H), 1.3—1.6 (t+s(δ 1.35), 4H), 3.05 (s, 1H), 3.55 (dd,J=7.5, 3 Hz, 2H)
4b[e]	90—100/2	3375, 1030, 830	0.5—2.5 (m+s (δ 1.17), 15H), 3.0 (br s, 1H), 3.56 (dd, J=7, 3 Hz, 2H)
4c[f]	120—125/5	3350, 1030, 850, 830	0.5—2.5 (m+s(δ 1.22), 17H), 2.8(br s, 1H), 3.60 (dd, J=7, 3 Hz, 2H)
4d[g]	140—150/0.08	3370, 1035, 855, 820	0.7—1.9 (m, 24H), 3.70 (dd, J=8, 1.5 Hz, 2H)
7[h]	140—150/7	3350, 3100, 1640, 1030, 998, 915, 854, 830, 807	1.0—2.4(m+s(δ 1.20), 8H), 2.6—3.2(br s, 1H), 3.70(d, 2H), 4.7—6.1 (m, 3H)
2[i]	120—140/140	1705, 1625, 1174	1.06 (d, J=6 Hz, 3H), 1.6—2.6 (m+s (δ 2.10), 6H), 5.80 (br s, 1H)
5b[j]	100—105/2	1702, 1649, 1345, 1300, 1073	0.7—2.0 (m+s (δ 1.63), 10H), 2.1—2.8 (m, 6H)
5c[j]	130—135/3	1698, 1650, 1384, 1340, 1302, 1072	0.6—1.9 (m+s (1.65), 12H) 2.0—2.7 (m, 6H)
9[k]	140—150/25[l]	3040, 1691, 1639, 1602, 1077, 962	1.73 (s, 3H), 1.95 (d, J=5.5 Hz, 3H), 2.1—2.9 (m, 8H), 6.3—6.9 (m, 2H)

a) Bath temperature. b) Neat liquid film. c) Measured in carbon tetrachloride solution. d) Found: C, 42.80; H, 6.13%. Calcd for $C_6H_{10}Cl_2O$: C, 42.63; H, 5.96%. e) Found: C, 53.24; H, 8.30%. Calcd for $C_{10}H_{18}Cl_2O$: C, 53.34; H, 8.06%. f) Found: C, 55.27; H, 8.69%. Calcd for $C_{11}H_{20}Cl_2O$: C, 55.24; H, 8.43%. g) Found: C, 61.43; H, 8.94%. Calcd for $C_{15}H_{26}Cl_2O$: C, 61.41; H, 8.92%. h) Found: C, 51.61; H, 6.93%. Calcd for $C_9H_{14}Cl_2O$: C, 51.69; H, 6.75%. i) Ref. 8. j) Ref. 24. k) MS *m/e*: 136 (M^+). Elemental analyses gave variable results due to the instability of this material. l) Distillation of the purified sample of **9** invariably gave resinous residue.

TABLE 4. PHYSICAL PROPERTIES OF DICHLOROHOMOALLYL ALCOHOLS

Compound	Bp (°C/Torr)[a]	IR(cm^{-1})[b]	PMR (δ)[c]
14c[d]	110—117/0.05	3450, 981, 936, 795	0.8—2.5 (m+s (δ 1.35), 17H), 5.34 (dd, J=10, 2 Hz, 1H), 5.70 (dd, J=16.5, 2 Hz, 1H), 6.38 (dd, J=16.5, 10 Hz, 1H)
14e[e]	99—106/0.05	3555, 3460, 1630, 984, 932, 790	1.1—2.2 (m, 15H), 5.24 (dd, J=10, 1 Hz, 1H), 5.65 (dd, J=16, 1 Hz, 1H), 6.25 (dd, J=16, 10 Hz, 1H)
14f[f]	110—115/0.09	3564, 3514, 1648, 980, 930	1.2—2.2 (m, 13H), 5.23 (dd, J=10, 1 Hz, 1H), 5.58 (dd, J=16, 1 Hz, 1H), 6.28 (dd, J=16, 10 Hz, 1H)

a) Bath temperature. b) Neat liquid film. c) Carbon tetrachloride solution. d) MS *m/e* (rel intensity): 155 (13), 153 (18), 129 ($M^+-Cl_2CH=CH_2$, 47), 69 (59), 43 (100). Found: C, 55.48; H, 8.52%. Calcd for $C_{11}H_{20}Cl_2O$: C, 55.24; H,8.43%. e) MS *m/e* (rel intensity): 201 (M^+-Cl, 2), 165 (11), 151 (15), 127 ($M^+-Cl_2CCH=CH_2$, 87), 109 (60), 81 (55), 67 (99), 55(100). Found: C,55.70; H, 7.54%. Calcd for $C_{11}H_{18}Cl_2O$: C, 55.71; H, 7.65%. f) MS *m/e*(rel intensity): 187 (M^+-Cl, 6), 113($M^+-Cl_2CCH=CH_2$, 100), 95 (93). Found: C, 53.75; H, 7.47%. Calcd for $C_{10}H_{16}Cl_2O$:C, 53.83; H, 7.22%.

nucleophile with Umpolung[19] of the carbonyl function. The latter methodology is highly effective for cyclopentenone annulation,[14,20] which involves addition of a three carbon chain followed by electrocyclic ring closure.[21-23]

Experimental

Distillation was carried out by use of Kugel-rohr (Buchi) and boiling points were determined by measuring the bath temperature. All the temperatures are uncorrected. PMR spectra (tetramethylsilane as an internal standard) were taken on a JEOL C-60H, Varian EM 360, or EM 390 spectrometer, chemical shifts being recorded in ppm unit. IR spectra were obtained on a Shimadzu IR-27G spectrometer in neat liquid film unless otherwise stated, MS on a Hitachi RMU-6L spectrometer, exact mass on a JEOL-JMS-D300 spectrometer. Tetrahydrofuran (THF) was freshly distilled before use over benzophenone ketyl. Commercially available hydrobromic acid (47%), chloroform, hexadecyltrimethylammonium bromide and butyllithium were used. Preparative TLC was prepared by use of Merck Kiesel-gel PF_{254}. Column chromatography was carried out with Wakogel C-100 (Wako Pure Chemical Co.).

Dichlorocarbene Addition to Allyl Alcohol. A Typical Procedure for 1. A mixture of 4-methyl-3-penten-2-ol (1.00 g, 10.0 mmol), chloroform (5.0 ml, 62 mmol) and hexadecyltrimethylammonium bromide (100 mg, 0.27 mmol) was heated at 50—55 °C, aqueous sodium hydroxide (0.60 g, 15 mmol, in 0.6 ml of water) being added drop by drop under vigorous stirring over a period of *ca.* 1 h. After addition was completed, the reaction mixture was maintained at the same temperature for 3 h and then cooled, neutralized with dil hydrochloric acid and extracted three times with dichloromethane. The organic phase was dried (Na_2SO_4), concentrated *in vacuo* and the residue distilled at 100 °C (bath temp)/45 Torr. The distillate (1.68 g, 92% yield) solidified and was recrystallized from hexane to give colorless needles (1.58 g) of **1**, mp 72—73 °C (Found: C, 45.76; H, 6.53%). Spectral data are in line with those recorded.[5] The characteristics of other adducts **4** are summarized in Table 3.

*Synthesis of 2-Methyl-3-pentyl-2-cyclopentenone (**5c**)*

Aqueous sodium hydroxide (1.5 g, in 1.5 ml of water) was added dropwise over a period of 15 min to a solution of 3-methyl-2-nonen-1-ol (**3c**) (880 mg, 5.64 mmol) and hexadecyltrimethylammonium bromide (50 mg) in chloroform (1 ml) under a nitrogen atmosphere at 55 °C. After being stirred for 3 h the mixture was neutralized with dilute hydrochloric acid and then worked up. Distillation at 120—125°C/5 Torr gave the adduct **4c** (806 mg, 60% yield). Spectral characteristics of **4c** are given in Table 3. The alcohol **4c** (476 mg, 2 mmol) was mixed with 47% hydrobromic acid (3 ml) and heated at 100 °C for 9 h. The reaction mixture was diluted with water and extracted with ether. The ethereal extract was washed with brine, aq sodium hydrogencarbonate solution, and finally with brine, dried (Na_2SO_4) and concentrated *in vacuo*. TLC purification of the crude product (silica gel, ether–hexane 3: 1, R_f 0.7) gave **5c** (196 mg, 59% yield, see Table 3).

*Synthesis of 2,3-Decamethylene-2-cyclopentenone (**5d**).* 2-(Cyclododecylidene)ethanol (342 mg, 1.62 mmol) was mixed with ethyl vinyl ether (1 ml) and dichloromethane (2 ml) containing pyridinium tosylate[10)] (50 mg) and the mixture was stirred for 1 h. The usual work-up gave an oil which was dissolved in chloroform (2 ml) containing hexadecyltrimethylammonium bromide (30 mg). To the resulting mixture was added sodium hydroxide (0.6 g in 0.6 ml of water) over a period of 15 min with vigorous stirring at 50 °C under an argon atmosphere. Stirring was continued for 4h, and the reaction mixture was diluted with water, neutralized with 5% hydrochloric acid and extracted with dichloromethane. The organic phase was dried (Na_2SO_4) and concentrated. The crude product was dissolved in ethanol (5 ml) in the presence of pyridinium tosylate (50 mg) at room temperature for 1 h. The work-up followed by short column chromatography (silica gel, dichloromethane elution) gave the desired adduct **4d** (366 mg, 77% yield).

The adduct **4d** (170 mg, 0.58 mmol) dissolved in TFA (5 ml) was heated to reflux for 90 h under an argon atmosphere. Concentration and preparative TLC of the residue (silica gel, dichloromethane) gave **5d** (R_f 0.3—0.45) (88 mg, 76%) along with an oil tentatively assigned as a trifluoroacetate of **4d** (R_f 0.95—0.98) (*ca.* 35 mg); IR (neat): 1794, 1225, 1160 cm^{-1}.

*Synthesis of [3-(3-Butenyl)-3-methyl-2,2-dichlorocyclopropyl]-methanol (**7**).* Sodium hydroxide (1.0 g) dissolved in water (1 ml) was added dropwise over 15 min at 40—50 °C to a mixture of the (*E*)-3-methyl-2,6-heptadien-1-ol (**6**) (504 mg, 4.0 mmol), chloroform (2.8 ml, 34 mmol) and benzyl(2-hydroxyethyl)dimethylammonium hydroxide (20 mg). After being stirred for 3 h at 50 °C, the reaction mixture was diluted with water (20 ml) and dichloromethane (20 ml). The aqueous phase was neutralized with dil hydrochloric acid and the organic phase was separated. The aqueous phase was extracted with dichloromethane (2×10 ml), organic phase being combined, washed with brine and concentrated *in vacuo*. Column chromatography on silica gel (benzene–ether 2: 1) gave the adduct **7** (450 mg, 57% yield, see Table 3).

Addition of 1,1-Dichloroallyllithium to Ketones. This reaction was carried out according to the reported conditions.[12a)] Physical properties of simple ketone adducts are given in Table 4.

*Synthesis of Bicyclo[10.3.0]pentadec-1(12)-en-13-one (**5d**).* The dichlorohomoallyl alcohol **14d** (105 mg, 0.36 mmol) was dissolved in TFA (1.3 ml) at room temperature and the solution was vigorously stirred for 1.5 h, the color tunring from light red to dark red. The work-up was effected by adding ether (10 ml), neutralizing with aq sodium hydrogencarbonate solution and by extracting with ether (4×20 ml). The ethereal solution was dried (Na_2SO_4), and concentrated *in vacuo* to give an oil which was purified by preparative TLC (silica gel, dichloromethane–ether 10: 1, R_f 0.3—0.5), affording **5d** (71 mg, 90% yield). PMR: δ 0.9—1.9 (m, 16H), 1.9—2.6 (m, 8H); IR: 1690, 1634 cm^{-1}; MS *m/e* (rel intensity): 220 (M^+, 65), 177 (93), 163 (98), 149 (100), 110 (65).

*Synthesis of 3-*t*-Butylbicyclo[4.3.0]non-1(6)-en-7-one (**15**).* At −78 °C lithium diisopropylamide (15 mmol) in THF (10 ml) was added drop by drop over a period of 2 h to a THF (20 ml) solution of 4-*t*-butylcyclohexanone (1.54 g, 10.0 mmol) and 3,3-dichloropropene (1.33 g, 12.0 mmol) under an argon atmosphere. After the addition was completed the resulting dark purple solution was stirred for 80 min at −78 °C and then treated with methanol (2 ml) at −78 °C. The mixture was warmed to room temperature, treated with water (*ca.* 50 ml) and extracted with ether (4×20 ml). The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane–ether 50: 3) to give the desired adduct (1.42 g, mp 100.8—101.1 °C (hexane), 54% yield, 76% yield based on the consumed ketone) and the starting material (0.45 g). The adduct showed the following spectra. PMR: δ 0.83 (s, 9H, *t*-Bu), 1.0—2.1 (m, 10H), 5.32 (dd, J=10, 1 Hz, 1H), 5.68 (dd, J=16, 1 Hz, 1H), 6.31 (dd, J=16, 10 Hz, 1H). IR: 3480, 981, 964, 933 cm^{-1}. Found: C, 59.02; H, 8.35%. Calcd for $C_{13}H_{22}Cl_2O$: C, 58.87; H, 8.36%.

The adduct (537 mg, 2.0 mmol) was mixed with THF (3 ml) at room temperature and the solution was stirred for 2.5 h. The work-up followed by preparative TLC (silica gel, hexane–ether 1: 1) gave the desired **15** (279 mg, 72% yield). Bp 102—110 °C (bath temp)/0.05 Torr. PMR: δ 0.93 (s, 9H, *t*-Bu), 1.1—2.6 (m, 11H); IR: 1692, 1658 cm^{-1}; MS *m/e* (rel intensity): 192 (M^+, 27), 164 (8), 136(74), 57 (100). Found: C, 80.91; H, 10.65%. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48%.

*Synthesis of 6-Methylbicyclo[5.3.0]dec-1(7)-en-8-one (**16**).* Under a nitrogen atmosphere at −78 °C, lithium diisopropylamide (15 mmol in THF 10 ml) was added drop by drop over 1.75 h to a THF (15 ml) solution of 2-methylcycloheptanone (1.26 g, 10.0 mmol) and 3,3-dichloropropene (1.33 g, 12.0 mmol), and the reaction mixture was stirred for 1.5 h at −78 °C and worked up. Column chromatography (silica gel, hexane–ether 20: 1) of the crude product gave the desired adduct (1.19 g, 50% yield). The adduct was apparently homogeneous as evidenced by PMR spectrum and TLC assay (silica gel, hexane–ether, 1: 1, R_f 0.63). Bp 118—124 °C (bath temp, partial decomposition)/0.05 Torr. PMR: δ 1.0—2.9 (m+d (δ 1.05, J=6.0 Hz), 15H), 5.25 (dd, J=10, 1 Hz, 1H), 5.68 (dd, J=16, 1Hz, 1H), 6.29 (dd, J=16, 10 Hz, 1H); IR: 3550, 3475, 982, 930 cm^{-1}; MS *m/e* (rel intensity): 236 (M^+, 1), 201 (11), 187 (29), 165 (28), 152 (28), 127 (47), 109 (74), 67 (89), 55 (100). Correct elemental analysis was not achieved due to partial decomposition on distillation.

The adduct (341 mg, 1.4 mmol) was dissolved in TFA (4 ml) at room temperature and the resulting solution was kept at room temperature for 6 h and at reflux temperature for 18 h. The work-up followed by preparative TLC (silica gel, hexane–ether, 2: 1, R_f 0.2—0.3) gave the desired product **16** (138 mg, 58% yield). Bp 122—128 °C (bath temp)/3 Torr. PMR: δ 0.96 (d, J=7.0 Hz, 3H), 1.1—2.1 (m, 6H), 2.1—3.2 (m, 7H); IR: 1689, 1638 cm^{-1}; MS *m/e* (rel intensity): 164 (M^+, 100), 149 (88), 136 (64), 122 (58), 107 (70), 93 (80). Found: C, 80.40; H, 10.08%. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82%.

Addition of 1,1-Dichloroallyllithium to 2-Methylcyclohexanone. Lithium diisopropylamide (23.0 mmol prepared from diisopropylamine (3.2 ml) and butyllithium (1.81 M hexane solution, 13.3 ml) in THF (15 ml) at 0 °C) was added drop by drop at −78 °C under a nitrogen atmosphere to a THF (20 ml) solution of 2-methylcyclohexanone (1.67 g, 14.9 mmol) and 3,3-dichloropropene (2.00 g, 18.0 mmol) over a period of 2 h, and the resulting solution was stirred for another hour at −78 °C until quenching with methanol (1 ml) at −78 °C. The work-up followed by column chromatography (silica gel, hexane–ether 20: 1) gave the adduct **18** (0.94 g, 28% yield). Bp 126—131 °C (bath temp)/4 Torr. PMR: δ 0.75 (d, J=7.0 Hz, 3H), 0.9—2.7 (m, 10H), 4.12 (d, J=7.0 Hz, 2H), 6.15 (t, J=7.0 Hz, 1H); IR: 3480, 1642, 988, 850, 785 cm^{-1}; MS m/e (rel intensity): 226 (M$^+$ +4, 3), 224 (M$^+$ +2, 5), 222 (M$^+$, 19), 187 (54), 173 (86), 152 (75), 117 (69), 95 (72), 68 (100); Exact mass; 222.0561, 224.0533, 226.0514. Calcd for $C_{10}H_{16}Cl_2O$: 222.0577 (M$^+$), 224.0548 (M$^+$ +2), 226.0519 (M$^+$ +4). Elemental analysis gave an error of 0.46% for C probably due to partial decomposition on distillation.

The alcohol **18** (192 mg, 0.86 mmol) was dissolved in TFA (1.5 ml) and the solution was stirred at room temperature for 2.5 h. The work-up gave the hydroindanone **19**[18] (61 mg, 47%). PMR: δ 1.06 (d, J=6.0 Hz, 3H), 1.2—2.0 (m, 4H), 2.0—2.8 (m, 7H); IR: 1690, 1639 cm^{-1}; MS m/e (rel intensity): 150 (M$^+$, 83), 135 (39), 122 (48), 108 (96), 93 (100), 79 (65).

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